## CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD SAN FRANCISCO BAY REGION

ORDER NO. 94-015

CEASE AND DESIST ORDER

SHELL OIL COMPANY

Martinez, Contra Costa County

UNION OIL COMPANY OF CALIFORNIA

Rodeo, Contra Costa County

EXXON COMPANY, U.S.A.

Benicia, Solano County

The California Regional Water Quality Control Board, San Francisco Bay Region (hereinafter called the Regional Board) finds that:

- 1. Shell Oil Company ("Shell"), Union Oil Company of California ("Unocal"), and Exxon Company, U.S.A. ("Exxon"), hereinafter collectively referred to as the dischargers, operate petroleum refineries that discharge wastewater into the Carquinez Straits and Suisun Bay.
- 2. On February 20, 1991, the Regional Board issued Order No. 91-026 amending the dischargers' existing National Pollutant Discharge Elimination System (NPDES) Permits to include a concentration-based effluent limitation for selenium of 50 ppb (daily maximum) and a mass-based limitation, expressed in pounds per day, equivalent to 50 ppb times the flow rate for each discharger, as determined on an annual average basis. These limitations, referred to as Individual Control Strategies (ICS), were issued to the dischargers pursuant to state authority under the NPDES program and as a result of the "short listing" of San Pablo Bay, Carquinez Strait and Suisun Bay (hereinafter generally referred to as "the Bays") under section 304(l) of the federal Clean Water Act as impaired water bodies for selenium. The listing decision was made by the U.S. Environmental Protection Agency on September 28, 1990.

3. The 1986 Basin Plan for the San Francisco Bay Region established effluent limitations for discharge to the estuary based on the lower of fresh or salt water objectives, due to fluctuating salinities. The 1986 Basin Plan also established the pattern of calculating effluent limitations for deep water dischargers based on a dilution credit of 10:1. In other words, the adopted effluent limitations for deep water discharges were, for the most part, ten times the objective. In 1987, the US Environmental Protection Agency promulgated water quality criteria for selenium, based on the protection of aquatic life, of 5 ug/L for fresh waters, and 71 ug/L for marine waters, as four day average values. On April 11, 1991 the State Water Resources Control Board adopted the Inland Surface Waters Plan and the Enclosed Bays and Estuaries Plan, which established water quality objectives for selenium of 5 ug/L for fresh waters and 71 ug/l for marine waters, and stated that the objectives in the Inland Surface Waters Plan shall apply to freshwater portions of enclosed bays and estuaries. On September 16, 1992 the Regional Board adopted amendments to the Basin Plan. These amendments established that the dilution credit for deep water discharges is limited to 10:1, and established an effluent limitation of 50 ug/L for selenium for deep water discharges for both fresh and marine waters. The reliance on the fresh water objective for the entire estuary was based on the potential for bioaccumulation of selenium, evidenced in part by the health advisory limiting consumption of diving ducks from Suisun Marsh, due to elevated tissue levels of selenium. These portions of the Basin Plan amendments were approved by the State Water Resources Control Board on April 27, 1993 and have not yet been considered by the Office of Administrative Law.

On December 22, 1992, the US Environmental Protection Agency issued a final rule (40 CFR 131.36), also known as the National Toxics Rule, which established a criteria of 5 ug/L for the waters of San Francisco Bay to and including Suisun Bay and the Sacramento-San Joaquin Delta. The final rule states that "the fresh water selenium criteria are included for the San Francisco Bay estuary because high levels of bioaccumulation of selenium in the estuary indicate that the salt water criteria are underprotective for San Francisco Bay". This rule became effective February 5, 1993.

- 4. The effluent limitations imposed under Order No. 91-026 become effective on December 12, 1993. For reasons explained below, the dischargers will not be able to achieve compliance with the selenium limits by the date specified in Order No. 91-026 and are therefore threatening to violate the order. The Regional Board is adopting this Order to enforce the provisions of Order No. 91-026.
- 5. On June 19, 1991, the Regional Board issued Order No. 91-099, further amending the dischargers' NPDES permits to include immediately effective interim selenium discharge limits calculated on the basis of each refinery's "current performance," as defined in the order. These interim limits continue to apply until the limits imposed in Order No. 91-026 are achieved.

- 6. The Western States Petroleum Association ("WSPA") and the six Bay Area refiners (Shell, Unocal, Exxon, Chevron, Tosco and Pacific Refining) filed a Petition for Review with the State Water Resources Control Board on March 22, 1991, challenging the issuance of the ICS's and the underlying listing of the Bays under Section 304(l) of the Clean Water Act on the grounds that the "applicable water quality standard," as defined under section 304(l), was not violated in the Bays and that the Board's action in issuing the ICS's was unlawful and improper. Petitions for Review were also filed by Citizens for a Better Environment and the Pipe Trades Council of Northern California. On September 16, 1992, the State Board dismissed without prejudice all Petitions for Review, stating that the Regional Board was scheduled to consider the issues raised in the petitions, including site-specific objectives for selenium in the designated water bodies and schedules for compliance with the objectives.
- 7. On October 16, 1992, WSPA and the six Bay Area refineries filed a Petition for Writ of Mandate in Superior Court for the County of Solano, seeking to set aside the ICS's and the underlying Clean Water Act listing of the Bays. This action is currently pending, but will be dismissed upon adoption of this Order.
- 8. In 1987, Chevron was required to determine the source of selenium in its effluent and develop all reasonable measures to limit selenium discharge as a condition of its NPDES permit. In 1990, Shell, Unocal, Exxon, and Pacific Refining were required to investigate and evaluate all feasible source control measures, process changes, and treatment options for reducing selenium effluent concentrations to 1, 10, and 50 ppb pursuant to their NPDES permits. These studies determined that the primary source of selenium in refinery effluent was the crude oil. A natural component of the crude, selenium is found in varying levels in different types of crude. The heavy crudes produced in the San Joaquin Valley of California contain high concentrations of selenium (~400-600 ppb) relative to crudes from other parts of the world (~50-250 ppb). For the most part, the Bay Area refineries have been designed to use San Joaquin Valley heavy crude for a significant percentage of their total crude intake.

The Regional Board reviewed information presented by the dischargers and has determined that a combination of process and treatment options are the most likely means of achieving the required loading reductions in the shortest period of time. This conclusion was based on an estimate that the maximum possible emission reduction that could be achieved by crude substitution would likely be less than required loading reductions, would take longer to accomplish, and would result in adverse economic impacts to oil producers and the surrounding community, compared to the proposed treatment technology implementation schedule.

- 9. Despite extensive research and testing by the six Bay Area refiners at a cost exceeding \$5 million, at present there is no known technology that is capable of removing selenium from refinery wastewater in a manner that does not produce large quantities of hazardous waste. The only technologies that have been shown to have any promise (iron co-precipitation and selective resin adsorption) would generate very large quantities of selenium-laden sludge (as much as 14 tons per day, depending on the refinery) which would be classified as a hazardous waste in California. The sludge would be subject to land disposal restrictions under the state Hazardous Waste Control Law and would itself have to be treated to remove or stabilize the selenium prior to land disposal.
- 10. In addition, after bench- and pilot-scale testing, neither iron co-precipitation nor selective resin adsorption has been shown to be effective in reducing selenium in refinery wastewater to 50 ppb on a consistent basis for all refineries.
- 11. WSPA has commenced a \$1.3 million research study (hereinafter called the "Technology Study") in a further, more comprehensive effort to identify a technology or technologies that are capable of removing selenium from refinery wastewater in a reliable and environmentally acceptable manner. The Technology Study consists of selenium speciation studies, selenium source studies, selenium fate studies and selenium removal studies, as described below.

As discussed in WSPA's proposal to the Regional Board staff, the form of selenium in the sour water and stripped sour water is still not fully understood. The first phase of this project will attempt to identify or at least characterize the selenium in these streams, as well as develop or refine techniques for quantifying the selenium species most likely to be present. Knowledge of the selenium species is critical to developing and improving the effectiveness of promising selenium removal processes. Speciation work under the WSPA study began in August 1993 and is being performed by Brown and Caldwell, with subcontracts to the California Public Health Foundation and ANC Research Laboratories. Procedures have been developed and tested on effluent samples for fractionation and quantification of various selenium forms (particulate selenium, neutral- and acidvolatile selenium, and anionic selenium species--selenite, selenate, and selenocyanate). A final report describing the method is currently being prepared by Brown and Caldwell and will be available for use in the technology development studies. SSW and final effluent samples are currently being analyzed using the speciation method developed.

The process development studies are intended to identify, develop, and demonstrate improvements in the most promising processes that would render them feasible as well as effective. The processes to be developed further include several of the various iron processes (ferric co-precipitation on SSW and biotreater effluent, elemental iron treatment of SSW, and the Unipure process on SSW),

alumina (Sorbplus treatment of SSW, and activated alumina treatment of SSW and final effluent), and ion exchange processes.

For the iron process, a suitable pretreatment process (eg. chemical oxidation) for the SSW stream needs to be developed to convert the selenium into the proper species for sorption onto the iron. Treatment of the SSW stream instead of the final effluent would allow for a significant reduction in the volume of water to be treated and the amount of sludge generated. Also, a method for regeneration/reuse of the iron sludge needs to be developed. Preliminary tests conducted by one refinery indicate that sludge washing at high pH may remove greater than 95% of the selenium sorbed to the spent iron sludge. The refineries have no experience with this type of sludge regeneration, and additional testing needs to be done to demonstrate its effectiveness. Finally, a process for treatment or disposal of the small-volume waste stream produced from the regeneration process needs to be developed. Proposals for this work were received in October 1993 and Brown and Caldwell was selected as the contractor. This part of the project is expected to be complete by October 1994.

For the alumina and ion exchange processes, either a pretreatment step needs to be developed to remove chemical species that compete with selenium for sorption sites, thereby increasing the sorption capacity of the ion exchange material, or regeneration processes need to be developed that would allow the sorbent to be reused. Proposals for study of the ion exchange and alumina processes are currently under review, and a contract will be issued by WSPA in early 1994. Expected completion date for this portion of the project is December 1994.

The WSPA effort will also include a study of biological treatment options for selenium removal. Two approaches will be evaluated—an anaerobic system that converts selenate and selenite to elemental selenium and an aerobic system that converts selenite into cell-bound elemental selenium. The latter has the potential to be used as part of an aerobic treatment system treating selenium-containing stripped sour waters. Montgomery-Watson, the oversight contractor, is currently developing a scope of work to pursue these two approaches. WSPA plans to select a contractor for these studies during spring 1994.

These studies are being conducted on a staggered schedule, with a final completion and reporting date of July 1995. The studies will be expedited, if possible. This schedule is consistent with the two-year duration study originally estimated in WSPA's research proposal. At the conclusion of the study, each refiner will select an appropriate technology (or technologies) for pilot evaluation based on its effectiveness, feasibility, and cost. Pilot-scale testing will be performed on-site at each refinery, and managed separately by each individual refiner. Pilot test result will be shared and reported on a regular basis to the Regional Board. This will maintain communication lines, and assure that troubleshooting and process

refinement efforts are not duplicated. Pilot testing, including design, construction, operation and reporting, is expected to take approximately one year. After successful outcome of a pilot-scale test, the design, engineering, construction and start-up of a full-scale unit is expected to take about two years on an accelerated schedule.

- 12. WSPA has convened a Task Force for the purpose of monitoring the progress of the Technology Study. Staff of the Regional Board are participating in the Task Force.
- 13. The Regional Board has proposed an amendment to the Water Quality Control Plan for the San Francisco Bay Region (Basin Plan) which would establish an industry wide, mass emission reduction strategy (MERS) for selenium which is targeted at a level below 50 ppb. The schedule for selenium reductions in the MERS, if adopted, or in any other amendment to the Basin Plan, will not be inconsistent with the schedule for compliance contained in this Order.
- 14. The Regional Board, WSPA, and the dischargers have reached a settlement of the litigation described in paragraph 7. That settlement includes a term providing that the dischargers shall pay the Regional Board the sum of \$1 million within 30 days of adoption of this Order and \$1 million on January 31, 1995. The Regional Board has considered the various enforcement and penalty options available to it regarding violation of Order No. 91-026, including the issuance of a cease and desist order or a cleanup or abatement order, imposition of an administrative civil penalty and referral to the Attorney General for civil prosecution. Under the circumstances detailed in the Findings set forth above, the Regional Board has determined that the most appropriate course of action is settlement of the litigation and issuance of a cease and desist order.
- 15. This Order is an action to enforce the laws and regulations administered by the Regional Board. This action is categorically exempt from the provisions of the California Environmental Quality Act (CEQA) pursuant to Section 15321, Title 14, California Code of Regulations.
- 16. The Regional Board has notified the dischargers and interested agencies and persons of its intent under California Water Code Section 13301 to consider the adoption of a Cease and Desist Order for the threatened discharge and has provided them with an opportunity for a public hearing and an opportunity to submit their written views and recommendations.
- 17. The Regional Board, in a public hearing, heard and considered all comments pertaining to the threatened discharge.

IT IS HEREBY ORDERED, pursuant to Section 13301 of the California Water Code, that Shell Oil Company, Union Oil Company of California, and Exxon Company, U.S.A. shall cease and desist from discharging waste in violation of Order No. 91-026 by complying with the following:

- 1. The dischargers shall ensure implementation of the Technology Study or a comparable study. The goal of such study is to identify suitable technologies capable of removing selenium from refinery discharges. The scope of the study shall encompass evaluation of all promising technologies, including those which might be capable of achieving concentration-based limits significantly below 50 ppb, identify the most feasible of these, and communicate the precise decision criteria by which feasibility was determined.
- 2. The dischargers shall ensure that the Task Force make reports to the Regional Board every six months on the progress of the Technology Study and share such other information concerning control of selenium as may become available. These reports shall at a minimum describe a) the status of the most promising technologies; b) decisions made since the previous progress report regarding continuing or discontinuing research on a particular technology and the rationale for doing so; c) summary of work at individual refineries relevant to and/or used during the Technology Study including but not limited to studies addressing selenium mass balances throughout individual refinery systems, the fate and removal of selenium in currently operating biological treatment systems, pilot scale studies, and any other research conducted at individual sites; and d) projected schedules and status of pilot tests and implementation measures at each refinery. These reports shall be presented by the dischargers at public meetings or workshops as determined by the Executive Officer.
- 3. Compliance with this Order shall be in accordance with the following tasks and time schedules:
  - a. The dischargers shall complete the Technology Study or a comparable study no later than July 31, 1995.
  - b. The dischargers shall initiate pilot tests of candidate selenium removal technologies or alternate control strategies no later than December 31, 1995.
  - c. The dischargers shall implement a removal technology or technologies, or an alternate control strategy, which has been determined by the dischargers to be capable of achieving compliance with the discharge limitations as specified in Order No. 91-026 and shall comply with these limits, no later than July 31, 1998.

d. In addition to evaluating treatment options through the Technology Study, the dischargers shall also evaluate and report on all promising process changes which may also significantly reduce selenium mass discharge. At a minimum, each refinery shall evaluate and report on selenium mass emission reduction by (a) using recycled sour water in existing or planned coking systems; (b) enhancing the removal efficiency of existing biotreatment systems; and (c) reuse of sour water and other selenium-containing waste streams in any other appropriate processes.

Each discharger shall submit a schedule to the Regional Board by April 1, 1994 for evaluating and reporting on (a), (b), and (c) above.

- 4. In the event a discharger is successful in identifying and piloting a workable selenium removal technology or other control strategy in advance of the schedule set forth in Provision 3, the discharger shall, to the extent feasible, accelerate the implementation of such technology or control strategy so as to achieve compliance with the 50 ppb limit in advance of the July 31, 1998 deadline.
- 5. In the event a discharger is unable by July 31, 1998, to identify or implement a workable removal technology or other control strategy, either through the Technology Study or its own internal efforts, an extension of the final compliance date will be considered and may be granted based on information regarding technological availability and demonstration of a good faith effort to achieve compliance.
- 6. During any period of extension granted under Provision 5, the discharger shall continue to use all reasonable efforts to identify or implement a workable selenium removal technology or other control strategy, consistent with the efforts required by this Order. The discharger shall provide the Regional Board with quarterly status reports on its progress in achieving compliance.
- 7. If the Executive Officer finds that the dischargers have failed to comply with the provisions of this Order, he is authorized after approval of the Regional Board Chairman, to request the Attorney General to take appropriate action against the dischargers, including injunctive and civil remedies, if appropriate, or to issue a Complaint for Board consideration of Administrative Civil Liabilities.
- 8. Each discharger shall maintain a copy of this Order at its facility so as to be available at all times to facility operating personnel.
- 9. If any discharger is delayed, interrupted or prevented from meeting one or more of the time schedules in this Order due to circumstances beyond their reasonable control, the discharger shall promptly notify the Executive Officer. In the event of such delays, the Regional Board will consider modification of the time schedules

established in this Order.

- 10. This Order shall be effective on January 19, 1994.
- I, Steven R. Ritchie, Executive Officer, do hereby certify the foregoing is a full, true and correct copy of an Order of the California Regional Water Quality Control Board, San Francisco Bay Region, on January 19, 1994.

STEVEN R. RITCHIE Executive Officer